HYDROGENOLYSIS OF BENZENE AND ALKYLATED
BENZENES OVER COAL CHARS

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INTRODUCTION

The Research Triangle Institute (RTI) is conducting an experimental study to assess the environmental impacts of coal gasification and evaluate control technologies for the many potential pollutants that are formed during gasification. Pollutant generation behavior of 10 U.S. coals has been studied in a bench-scale gasifier under a variety of conditions (1-3). Process operating conditions such as continuous versus batch operation, fixed versus fluidized bed operation, temperature, coal type, pressure and particle size have been found to determine production behavior. Of major interest are the polycyclic aromatic hydrocarbons (PAH) and phenolic compounds.

Significant quantities of char or high ash solids are produced during coal gasification. One objective of this study was to determine the feasibility of using coal char as a catalyst to facilitate cracking of potential environmental pollutants. The authors are aware of only one previous study, which reported on decomposition of phenolics over lignite char (4). It was found that the presence of coal char greatly enhanced the decomposition of phenol. Virk, et al. (5) reviewed the literature on thermal hydrogenolysis of aromatic compounds. Benzene decomposition was slowest and anthracene decomposition was fastest among the various compounds studied (1 to 4 rings). No alkylated aromatics were reported upon, although various other studies (6-9) have been carried out on thermal hydrodealkylation of aromatics and phenols. In general, these studies agree with the mechanism originally proposed by Silsby and Sawyer (6) which results in a first order dependence of the rate on the concentration of the decomposing compound and half order dependence on hydrogen concentration with hydrogen dissociation at equilibrium. According to this mechanism, the cracking of alkylated aromatics and phenols seems to involve the benzene ring as an intermediate.

From the above discussion, it follows that benzene could serve as a model compound for comparing the catalytic hydrogenolysis potential of various coal chars. In addition to benzene, alkylated benzenes (toluene, ethylbenzene and o-xylene) were also chosen as model compounds for this study.

EXPERIMENTAL

The proximate and ultimate analysis of the char solids chosen for this study are shown in Table 1. The Wyoming subbituminous and the Illinois No.6 chars were produced by the steam-air gasification of the coals at 900°C and 200 psig in the RTI bench-scale gasifier. The Peabody char was obtained from Peabody Coal Company (Columbia, Tennessee) who prepared it by coking a Western Kentucky No.11 coal at 870 to 1090°C. For comparison, quartz and molecular sieve 4A were also used in the microreactor experiments. Representative samples of all materials were crushed and screened to 28 x 48 mesh. Microreactors were prepared as shown in Figure 1 with the volume of packing material being approximately 1 cm^3 and ranging in weight from 0.5 to 1.0 gram. A reactant gas containing 290 ppm benzene, 52.2 ppm toluene, 9.87 ppm ethylbenzene and 11.4 ppm o-xylene in nitrogen was used in all experiments. Hydrogen of high purity was blended with the reactant gas to obtain a hydrogen level of 50 percent. Details of the reactor flow system are shown in Figure 2. Gas residence time in the reactors ranged from approximately 0.25 to 0.5 seconds; and all experiments were carried out at slightly above atmospheric pressure. In the experiments utilizing coal chars the packed

TABLE 1. PROXIMATE AND ULTIMATE ANALYSIS OF CHARS

| | Weight % As Received | | |
	Peabody Char	Illinois No.6 Char	Wyoming Subbituminous Char
Proximate			
Moisture	1.46	0.77	1.27
Volatile Matter	1.73	2.56	5.89
Fixed Carbon	84.61	39.94	36.03
Ash	12.20	56.73	56.81
Ultimate			
Carbon	82.34	39.61	40.53
Hydrogen	0.82	0.59	0.46
Nitrogen	1.17	0.72	0.44
Sulfur	2.06	1.56	0.48
Oxygen (by difference)	1.41	0.79	1.28

microreactor was conditioned overnight with the reactant gas-hydrogen mixture at 800°C. In the experiments utilizing quartz and molecular sieve packings and in the tests using an empty reactor conditioning was not carried out. This led to some interesting observations on the transient cracking activity. Reactor temperatures were varied from 500 to 800°C. Analysis of reactants and products were carried out by gas-liquid chromatography with an 8' x 1/8" stainless steel column containing Tris-1,2,3-cyanoethoxy propane on 80/100 mesh Chromosorb P operated with a helium carrier gas flow of 20 ml/min at 85°C oven temperature in a Perkin-Elmer 3920B gas chromatograph with a flame ionization detector; 1.0 ml samples were injected using a zero volume six-port stainless steel Carle valve, operated automatically with a valve actuator and a valve timer with a 16 minute cycle.

RESULTS AND DISCUSSION

In the present experimental study with benzene and three alkylated benzenes present in the feed gas, a full description of the kinetics would be extremely complex since so many possible parallel and series reactions can occur. To limit the complexity of the data analysis a simple first order decomposition of each component is assumed. This is probably reasonable for ethylbenzene and o-xylene, however, the assumption could lead to under-estimation of the benzene and toluene cracking rates since benzene and toluene production from ethylbenzene and o-xylene and benzene productionfrom toluene are ignored. Justification for the simplified analysis is that (1) the amount of ethylbenzene and o-xylene in comparison to benzene is small and should not contribute significantly to the apparent rate of benzene decomposition, (2) at high decomposition rates of benzene, ignoring benzene production from the other aromatics will result in small errors in the apparent rate of decomposition since the benzene concentration is almost six times that of any other component, and (3) an upper bound on the benzene decomposition rate can be estimated as discussed towards the end of this section.

In previous studies (4-9) of hydrocracking, hydrogenolysis or hydrodealkylation of aromatic compounds the data obtained are correlated using a first order rate with respect to the compound being decomposed and one-half order with respect to the hydrogen concentration. Since in all experiments of this study a constant hydrogen mole fraction was maintained and in large excesses, the rate can be

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expressed in terms of a pseudo first order rate constant containing the hydrogen term. Assuming a plug flow reactor with negligible change in gas volume with extent of decomposition, the integrated material balance under isothermal conditions for the ith component can be written as

$$k = \frac{1}{\tau} \ln \frac{C_{ii}}{C_{io}}$$ 1)

where τ = space time, sec.

C_{ii}, C_{io} = inlet and outlet concentrations of the ith species, g mole/cm^3.

k_2 = first order rate constant, sec^{-1}.

This equation was used to calculate the first order rate constants for all experiments in order that the relative activity of the packing material toward cracking of aromatics could be compared with the empty reactor activity and published homogeneous decomposition rates. For each packing material, rate constants were determined at a series of temperatures. Arrhenius plots of the first order rate constants for the individual compounds are shown in Figures 3 through 6 and are compared with existing literature data. Table 2 gives the least squares estimates of the pre-exponential factors and activation energies.

Examination of Figures 3 through 6 shows that the steady-state cracking activity obtained in the empty bed experiments is unusually high being on the order of 1 to 2 magnitudes greater than homogeneous first order constants reported in the literature. The empty bed experiments reported in this paper were carried out in reactors that had high surface to volume ratios (about 3-6 times those used in previous studies (4-11)). Also the activity appeared to increase rapidly with run time as seen in Figure 7. Apparently the surface of the stainless steel reactor is increasing in activity under the the reducing action of hydrogen and possibly carbon laydown (in some unknown form); and the activity reaches a steady-state value after extended time periods (on the order of 12-24 hours).

Comparing the steady-state empty bed constants to the first order rate constants associated with each char (which show no time dependent activity after overnight conditioning) it can be seen that the Wyoming and Illinois No.6 chars show enhanced cracking activity over the empty reactor. The Peabody char showed significantly lower activity and quartz had a lower initial activity than the empty bed demonstrating that the packing material blinded in part, the activity of the stainless steel reactor wall. Consequently the rate constants associated with the Wyoming and Illinois No.6 chars are significantly higher than the homogeneous rate constants and more than two orders of magnitude higher than the homogeneous rates reported previously in the literature. The higher activity of the Wyoming and Illinois chars over the Peabody char is likely to be due to their significantly higher ash contents, which are known to contain substantial quantities of silica and alumina.

Quartz was used in the microreactor for the purpose of comparison because it was initially thought that it would be relatively inert and would have a packed bed voidage similar to the chars. However, the initial activity of quartz showed rate constants at least an order of magnitude higher than homogeneous rate constants reported in the literature. Furthermore, the rate constants were observed to increase with run time at 748°C and over a 24 hour period the rate constants for benzene and toluene increased by an order of magnitude. The time dependent behavior of these constants are shown in Figure 7. The steady-state rate constants for benzene and toluene over quartz were 1.95 and 5.59 sec^{-1}, respectively. The initial rate constants for the decomposition of benzene and toluene over quartz were obtained by extrapolating the data by the method of Gangwal, et al.(12).
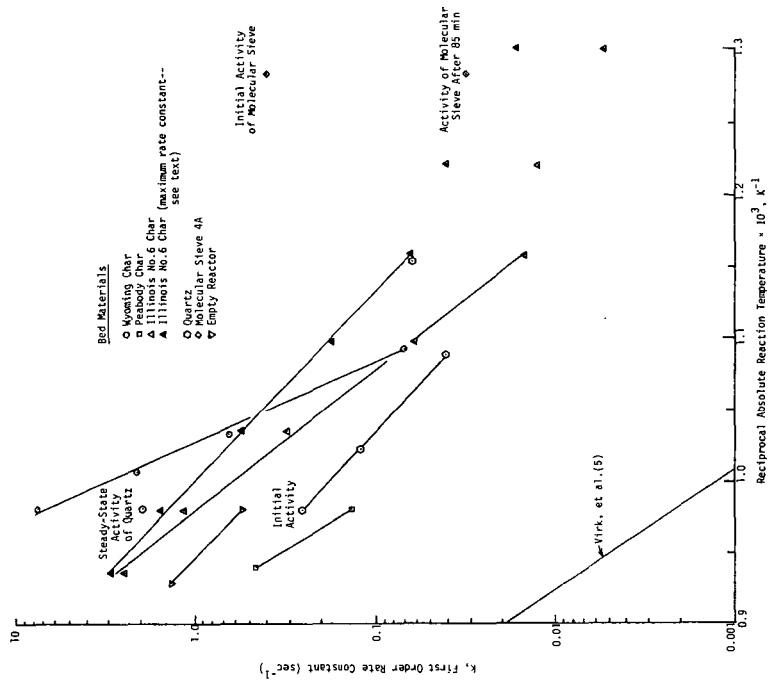
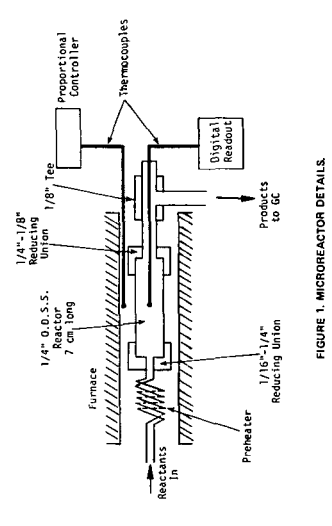## FIGURE 3 (Rate Constants for Benzene Hydrocracking)

Bed Materials

○ Wyoming Char
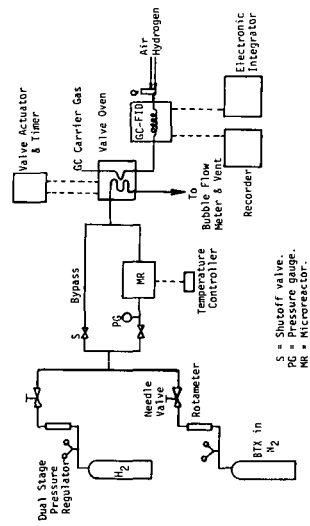□ Peabody Char
△ Illinois No.6 Char (maximum rate constant-- see text)

◇ Quartz
◇ Molecular Sieve 4A
▽ Empty Reactor

Initial Activity of Molecular Sieve

Activity of Molecular Sieve After 85 min

Steady-State Activity of Quartz

Initial Activity

Virk, et al.(5)

k, First Order Rate Constant (sec^{-1})

10   1.0   0.1   0.01   0.001

Reciprocal Absolute Reaction Temperature × 10^3, K^{-1}

0.9   1.0   1.1   1.2   1.3

FIGURE 3. RATE CONSTANTS FOR BENZENE HYDROCRACKING.

FIGURE 1

Proportional Controller

Thermocouples

Digital Readout

1/4"-1/8" Reducing Union

1/8" Tee

Products to GC

1/4" O.D.S.S. Reactor 7 cm long

1/16"-1/4" Reducing Union

Furnace

Preheater

Reactants In

FIGURE 1. MICROREACTOR DETAILS.

FIGURE 2

Valve Actuator & Timer

GC Carrier Gas

Valve Oven

Air

Hydrogen

GC-FID

Electronic Integrator

To Bubble Flow Meter & Vent

Recorder

Bypass

S

PG

MR

Temperature Controller

Dual Stage Pressure Regulators

H₂

Needle Valve

Rotameter

BTX in N₂

S = Shutoff valve.
PG = Pressure gauge.
MR = Microreactor.

FIGURE 2 REACTOR SYSTEM SCHEMATIC.

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FIGURE 5. RATE CONSTANTS FOR ETHYLBENZENE HYDROCRACKING.

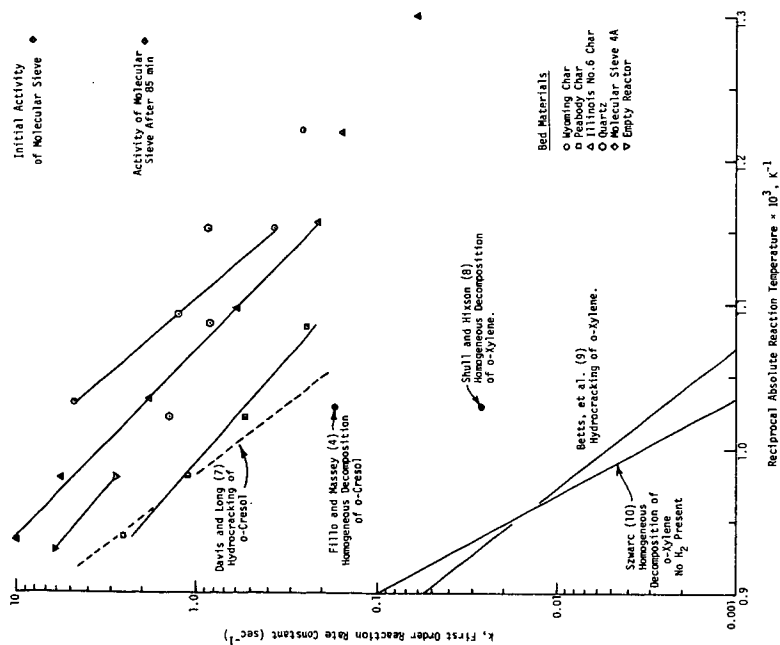**FIGURE 4. RATE CONSTANTS FOR TOLUENE HYDROCRACKING.**

Initial Activity of Molecular Sieve ◆

Activity of Molecular Sieve After 85 min ◆

Shull and Hixson (8) Homogeneous Decomposition of o-Xylene.

Betts, et al. (9) Hydrocracking of o-Xylene.

Davis and Long (7) Hydrocracking of o-Cresol

Fillo and Massey (4) Homogeneous Decomposition of o-Cresol

Szwarc (10) Homogeneous Decomposition of o-Xylene No H_2 Present

Bed Materials:
○ Wyoming Char
□ Peabody Char
△ Illinois No.6 Char
◇ Quartz
◇ Molecular Sieve 4A
▽ Empty Reactor

k, First Order Reaction Rate Constant (sec^{-1})

Reciprocal Absolute Reaction Temperature × 10^3, K^{-1}

FIGURE 6. RATE CONSTANTS FOR O-XYLENE HYDROCRACKING.

Toluene

Benzene

Benzene

Data Extrapolated by the Method of Gangwal, et al. (12)

0.640

0.256

Benzene

k, First Order Reaction Rate Constant, min^{-1}

Run Time, min

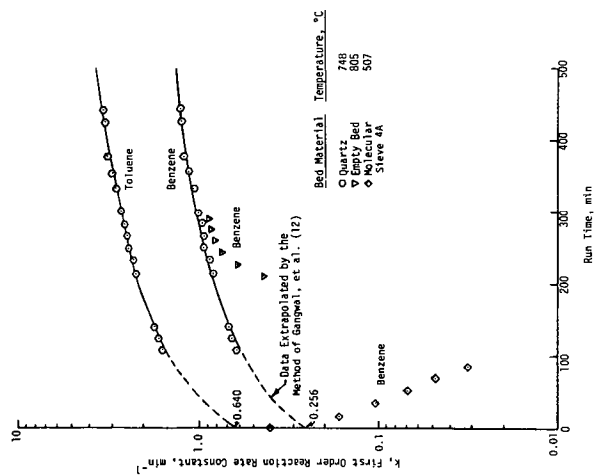| Bed Material	Temperature, °C
○ Quartz	748
▽ Empty Bed	805
◇ Molecular Sieve 4A	507

FIGURE 7. TIME DEPENDENT BEHAVIOR OF THE FIRST ORDER RATE CONSTANT.

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TABLE 2. ARRHENIUS EQUATIONS FOR HYDROCRACKING

Compound	Material	Arrhenius Equations $k = \quad (\sec)^{-1}$
Benzene	Wyoming Char	$1.71 \times 10^{18} \exp(-81290/RT)$
	Illinois No.6 Char[+]	$1.05 \times 10^{10} \exp(-46730/RT)$
	Peabody Char	$3.29 \times 10^{11} \exp(-57840/RT)$
	Quartz*	$4.61 \times 10^{6} \exp(-33920/RT)$
	Empty Reactor**	$3.38 \times 10^{7} \exp(-36510/RT)$
Toluene	Wyoming Char	$5.29 \times 10^{15} \exp(-68410/RT)$
	Illinois No.6 Char	$2.32 \times 10^{9} \exp(-41740/RT)$
	Peabody Char	$5.35 \times 10^{9} \exp(-47000/RT)$
	Quartz*	$2.98 \times 10^{2} \exp(-12360/RT)$
	Empty Reactor**	$7.21 \times 10^{6} \exp(-31250/RT)$
o-Xylene	Wyoming Char	$1.97 \times 10^{10} \exp(-42960/RT)$
	Illinois No.6 Char	$2.17 \times 10^{8} \exp(-35710/RT)$
	Peabody Char	$8.01 \times 10^{6} \exp(-31890/RT)$
	Quartz*	scatter
	Empty Reactor**	$1.75 \times 10^{7} \exp(-31830/RT)$
Ethylbenzene	Wyoming Char	$1.51 \times 10^{9} \exp(-34640/RT)$
	Illinois No.6 Char	$2.39 \times 10^{7} \exp(-29000/RT)$
	Peabody Char	$5.59 \times 10^{7} \exp(-34030/RT)$
	Quartz*	$8.05 \times 10^{4} \exp(-19610/RT)$
	Empty Reactor**	$2.06 \times 10^{10} \exp(-44830/RT)$

*Initial rate.
**Steady-state rate.
[+]Expression for maximum $k = 3.38 \times 10^{7} \exp(-36510/RT)$.

Material balances for carbon showed that carbon (in some form) was being deposited
on the quartz over the 24 hour run period. It is possible that the deposited
material was catalyzing the cracking of the benzene and toluene. After the 24
hour period at 748°C the temperature of the reactor was lowered to 650°C but
no enhancement in activity over previous experiments at 650°C was observed, i.e.,
whatever was being formed at 748°C was not active at 650°C.

    Molecular sieve 4A was also used as a packing material and showed very high
initial cracking activity in comparison to the other packing materials investi-
gated as can be seen in Figures 3 through 6. However, this activity quickly
faded as can be seen in Figure 7, with coke deposits blocking the porous structure
of the sieve being a probable deactivation mechanism.

    Based on the data presented in Figures 3 through 6 the following additional
observations can be made:

    1.   For a given volume of packing material and the same operating condi-
         tions the rate of cracking of the aromatic compounds is in the order

         ethylbenzene > o-xylene > toluene > benzene.

2. For a given aromatic compound and the same operating conditions with temperatures greater than 600°C, the activity of the char toward enhancing decomposition of compounds is in the order

Wyoming char > Illinois No.6 char > Peabody char.

The theoretical activation energy for homogeneous hydrodealkylation of alkylated aromatics is 50 ± 5 kcal/mole, based on the hydrogen dissociation mechanism originally proposed by Silsby and Sawyer (6). The experimental values reported are generally 45-50 kcal/mole for toluene hydrodealkylation (6-9). However, the empty bed activation energy for toluene (Table 2) is significantly lower, i.e., 31 kcal/mole, substantiating in part that the catalytic nature of the stainless steel reactor may be responsible. Virk, et al. (5) report an activation energy of 52.6 kcal/mole for homogeneous hydrogenolysis of benzene. Again the empty bed activation energy for benzene is much lower. The hetero- geneous hydrocracking reactions of benzene and toluene over the Wyoming char show significantly higher activation energies of 81 and 68 kcal/mole, respectively. The values are close to those reported by Szwarz (10) whose experiments were carried out in the absence of hydrogen. Thus the heterogeneous reaction may be proceeding by a mechanism which is entirely different from the homogeneous reaction. The Illinois and Peabody chars have activation energies associated with the decomposition of benzene and toluene which are considerably lower than those observed for the Wyoming char. One explanation for this is that the Wyoming char reaction rate is not limited by internal diffusion whereas the reaction rate for other chars might be. For an internal diffusion limited first order reaction the apparent activation energy is one-half of the true activation energy; this could explain in part the lower values observed for the Illinois and Peabody chars. This reasoning is supported by the experiments of Walker and coworkers (13-15) who have shown that low rank chars generally have an ample supply of feeder and transitional pores whereas bituminous and higher rank chars do not. The char samples used in this study have been sent to an outside testing laboratory for characterization of the pore structure and surface area. At the present time these results are not available; however, they will be reported at the presentation of this paper.

An upper bound on the benzene decomposition rate on Illinois No.6 char is shown in Figure 3 by the dark triangles. This is calculated assuming that benzene is an intermediate product from the cracking of the other aromatics present in the feed. When compared to the apparent rate (i.e., empty triangles) it can be seen that even higher rates of benzene decomposition exist if the assumption is true. The activation energy however is lower, i.e., 36.5 compared to 46.7 (see Table 2, footnote) and thus as the temperature increases the observed rate and the maximum possible rate approach each other.

The major gaseous product of decomposition of the aromatic compounds appeared to be light gases (probably mostly methane) although the GC column used in the experiment could not separate CH_4, C_2H_6 and C_2H_4. Much more methane was formed than could be accounted for by the removal of methyl groups from the alkylated benzene compounds. Also carbon balances showed that substantial quantities of the input carbon remained in the reactor. The only exception to this was in the case of the Wyoming char experiments run at 748°C and 800°C. In these cases carbon in the char also was converted to light gases (probably methane). The activation energy of this conversion was on the order of 104 kcal/g mole which corresponds to the temperature dependency of the equilibrium constant for hydrogen dissociation.

CONCLUSIONS

Based on the results obtained, it appears that coal-derived materials having high ash content show significant catalytic enhancement of the vapor

phase cracking of benzene and alkylated benzene compounds. It was found that the Wyoming subbituminous char showed significantly greater activity (as indicated by the first order reaction rate constants) than the Illinois and Peabody chars. The activity of the Peabody char was lower than the steady-state activity of the empty stainless steel reactor. The activity of stainless steel increased with time on stream to a steady-state activity that was an order of magnitude higher than the activity reported in the literature for the homogeneous decomposition of benzene and toluene.

ACKNOWLEDGEMENT

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